

STUDYING COAL MOLECULAR STRUCTURE WITH ELECTRON SPIN ECHO SPECTROSCOPY

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For several years, a major research goal of our laboratory has been the development of non-destructive spectroscopic techniques designed to study the molecular structure present in whole coal macerals. Our interest in this grows from our desire to know in more detail the microscopic structure of the organic components in coal in order to better determine the effects of various coal beneficiation technologies (e.g. various desulfurization techniques) on that structure. In this paper we wish to report on our progress using one very promising approach - Electron Spin Echo (ESE) spectroscopy. We will first briefly review the ESE technique and then present results obtained from Illinois #6 whole coal.

BACKGROUND

The physical and chemical characterization of whole coal by spectroscopic techniques presents several challenging problems. As Retcofsky points out in a good review of the applications of various spectroscopies to the coal system, the opaque, relatively non-volatile and insoluble nature of whole coal renders it a poor sample for conventional visible, UV, Raman, and mass spectrometry [1]. As a consequence of these difficulties, it has been customary to dissolve, extract, or volatilize coal prior to studying its atomic and molecular structure, and these pre-spectroscopic treatments have been shown to produce materials for examination that no longer represent the state of affairs in the whole coal itself. Magnetic resonance techniques (NMR, EPR, ESE, ENDOR) are not adversely effected by coal's physical properties, however, and these spectroscopies have played a role of ever increasing importance in coal characterization since 1954 when the first EPR spectrum of coal was obtained [2,3]. In particular, we know that new methods of performing the EPR experiment in the time domain hold exciting promise for the elucidation of the atomic and molecular structure of whole coal.

Electron Paramagnetic Resonance (EPR) looks at the energies associated with the magnetic dipole transitions of unpaired electrons. In coal, these unpaired electrons most often are associated with naturally occurring free radicals, which are present in all Illinois coals. While the stable free radicals in coal are interesting in themselves, they are of importance to our work in that they act as probes of the atomic environment in which they find themselves. Because of electron-nuclear dipole

interactions, the unpaired electrons "report" on the distance and orientation of neighboring nuclei with non-zero nuclear dipole moments (i.e. $I \neq 0$ nuclei) through the EPR signal. Such nuclei include hydrogen (^1H), carbon (^{13}C), and sulfur (^{33}S). Thus EPR is, in principle, able to give detailed information concerning the structure of coal. The excellent sensitivity of EPR (it can observe as few as 10^7 unpaired spins under favorable conditions) and the fact that it can be observed while subjecting coal to thermal and chemical treatments are other key benefits of studying coal by this spectroscopic technique.

In order to illustrate the main features of EPR spectra, and to gain insights into the characteristics of the EPR spectra from coal, let us consider a specific example. Figure 1 shows the EPR spectrum of a radical believed to occur naturally in coal [4]. This condensed ring aromatic, perylene, has three magnetically inequivalent protons which give rise to the complex and uniquely characteristic spectrum through their interaction with the unpaired electron of the radical. The excellent resolution of all the energies of interaction is due to the fact that the ion is freely tumbling in solution. If the species is immobilized by adsorption on a solid, a spectrum like that shown in Figure 2 results. Note that much of the resolution (detail) has disappeared. This spectrum no longer exhibits enough resolved information to identify the structure of the species giving rise to it; we will need somehow to extract the now unresolved information.

This example illustrates the key problem that needs to be addressed before EPR can be used to probe the atomic and molecular structure of coal. A new technique needs to be employed to resolve the important structural information that is obscured by so-called inhomogeneous broadening and various anisotropic interactions usually averaged to zero when the species are tumbling rapidly in solution. We have recently demonstrated that Electron Spin Echo spectroscopy (ESE) does, in fact, achieve this spectral resolution of the structural detail (hyperfine structure) from radicals in coal. Figure 3 is a Fourier transformed ESE spectrum of the adsorbed perylene radical showing the resolution of all three proton hyperfine couplings, including the weakest (about 2 MHz), which cannot be resolved by cw EPR [5]. This spectrum has the same format as an ENDOR spectrum, i.e.

$$f_i(\text{ENDOR}) = f(\text{proton}) \pm |A_i|/2, \quad 1)$$

where $f_i(\text{ENDOR})$ is the frequency of the i^{th} ENDOR transition, $f(\text{proton})$ is the precessional frequency of ^1H at the magnetic field of the experiment (in this case $f(\text{proton}) = 13.9 \text{ MHz}$) and $|A_i|$ is the absolute value of the i^{th} proton hyperfine coupling constant. In Figure 3, only the frequencies below the ^1H precessional frequency are shown.

ELECTRON SPIN ECHO SPECTROSCOPY

Although the ideas behind ESE techniques are as old as magnetic resonance itself (1946), the general application of spin echo methods to paramagnetic systems has occurred in only the last few years with the advent of very high speed digital electronics under computer control. Unlike the familiar continuous wave (cw) EPR experiment, which has been available in commercial instrumentation for nearly 20 years, ESE spectroscopy is not yet commercially available, and only a dozen or so laboratories throughout

the world currently perform the experiment. For an excellent review of the theory and early applications of ESE spectroscopy, the book by Kevan and Schwartz is recommended [6].

Unlike cw EPR, ESE is a pulsed microwave experiment. Very short microwave pulses excite the paramagnetic spin system, and the time evolution of the magnetization is monitored. Certain pulse schemes, characterized by the number of degrees the magnetization vector is tipped by each pulse, are known to generate a strong instantaneous magnetization in the sample following the sequence. Typical pulse schemes known to induce this rephasing or "echo" effect are $90^\circ - T - 180^\circ$ (Hahn echo sequence) and the $90^\circ - t - 90^\circ - T - 90^\circ$ (stimulated echo sequence). We have found the latter (stimulated echo) sequence to be most useful in our coal work. The sequence is diagrammed in Figure 4.

ESE spectroscopy has many advantages over the more conventional cw EPR. Chief among the advantages for our coal work is that the technique may be used to obtain spectra which resolve hyperfine structure that is obscured in cw spectra by inhomogeneous line broadening. In order to understand how ESE can be made to accomplish this task, let us look at the characteristics of the information obtained in the experiment.

In a typical stimulated echo experiment done on coal, the time interval t between the first and second 90° pulse is set at a fixed value during the experiment, while the interval T between the second and third pulses is incremented in steps, as shown in Figure 5. The amplitude of the echo induced by the sequence is measured as a function of the delay time T between the second and third pulses. In the absence of any interactions between the unpaired electrons being observed and neighboring nuclei with non-zero magnetic moments, the variation of the echo amplitude V with the delay time T is given by the simple exponential function:

$$V_{\text{echo}}(2t + T) = V_0 \exp \{-(2t + T)/T_m\}, \quad 2)$$

where T_m is the phase memory time of the individual spin packets. The exponential decay curve describing the echo amplitude as a function of T is called the electron spin echo envelope.

If our unpaired spins experience hyperfine interactions with neighboring nuclei, these interactions will manifest themselves as modulation patterns in the ESE envelope. This phenomenon is thus known as electron spin echo envelope modulation (ESEEM). For an $S = 1/2$ system with isotropic g -values (a very good approximation in the case of coal) and two hyperfine interactions characterized by frequencies f_a and f_b , the ESEEM pattern compensated for echo decay is given by:

$$V_{\text{mod}}(2t + T) = 1 - k[\sin^2(f_a t/2)\sin^2(f_b(t+T)/2) + \sin^2(f_b t/2)\sin^2(f_a(t+T)/2)] \quad 3)$$

In this expression, k is the so-called modulation depth parameter, proportional to B_0^{-2} in the limit of small hyperfine interactions (B_0 being the value of the static external magnetic field).

What makes the ESEEM effect so important to us is that a Fourier transform of the ESEEM pattern results in a frequency domain spectrum exhibiting linewidths that are characteristic of individual spin packets rather than of the entire envelope of spin packets comprising the inhomogeneously broadened lines observed by cw EPR. Since the modulation frequencies can be analyzed in an ENDOR-like theory, this technique provides us with a potential way of resolving the hyperfine interaction energies normally obscured in the cw spectra of whole coal. This information, in turn, allows us to study the environment experienced by radicals in coal, giving us a route to explore the atomic and molecular structure of whole coal. An example of a Fourier transformed ESEEM data set for the coal model system of perylene on alumina was shown in Figure 3.

Our typical experimental procedure when working on coal is to first carefully evacuate samples that have been ground to 50-100 mesh (although we have performed ESE experiments on large fragments). We have noticed that the presence of adsorbed oxygen has a significant effect on T_m , reducing it by more than a factor of two and making the experiments more difficult to perform; we have reported similar effects of oxygen on ENDOR spectra of coal [7]. Samples evacuated to pressures less than 10^{-6} Torr for several days are then sealed in quartz glass tubes for study. Experiments typically are performed at liquid helium temperatures in order to make T_m and T_1 as long as possible. A typical ESEEM result from an Illinois #6 coal is shown in Figure 6.

One can see in Figure 6 that the depth of the ESEEM pattern on the overall envelope is quite small. This is true for all coal samples. Since the signal-to-noise of the Fourier transformed spectrum is proportional to the modulation depth, we seek always to find ways to improve this feature of our ESE work. One obvious approach to improve matters is to recall that k , the modulation depth parameter from Equation 2, is proportional to B_0^{-2} . The spectrum shown in Figure 6 was taken at $B_0 = 3400$ G. on the spectrometer built by Norris and Bowman at ANL. We currently are building a spectrometer operating at $B_0 = 1000$ G. This instrument should improve the ESEEM amplitude by a factor of 10, and will be much better suited for the special characteristics of coal samples.

RESULTS AND DISCUSSION

The result of a stimulated echo experiment performed on powdered Illinois #6 coal was illustrated in Figure 6. Information on the proton hyperfine coupling constants of the species under observation now is present in the form of different periods of modulation that comprise the ESEEM pattern. In order to extract this data, the overall echo envelope may be simulated, making use of equations similar to that given in Equation 3. Alternately, the echo envelope decay function can be subtracted from the data and the remaining ESEEM function can be Fourier transformed to generate a frequency domain spectrum similar to that obtained from a cw ENDOR experiment. The advantage of the latter data processing route is that the result is in a familiar spectral format; one difficulty is that the amplitudes and phases of the spectral lines obtained in this way may be very unreliable.

Recently, Barkhuijsen, et. al. published a technique for analyzing ESEEM data that may combine the best features of both the simulation and FT approaches [8]. Called LPSVD (linear prediction singular value

decomposition), the analysis first simulates the ESEEM data using a linear combination of exponentially damped sinusoidal functions. The frequency, amplitude, T_M , and phase data for each component is then used to construct a new data set which then may be Fourier transformed to give a "noise-free" frequency domain spectrum. We currently are studying this analysis technique, and a more efficient variation of it called LPQRD [9]. Figure 7 illustrates the result of processing the ESEEM data of Figure 6 by the LPQRD method.

Analysis of the spectrum shown in Figure 7 is by the standard ENDOR formula given in Equation 1. For proton couplings, we expect to find pairs of lines symmetrically positioned about the free precessional frequency of the proton, $f(\text{proton})$, which is marked by an arrow labeled ^1H . Three such pairs of lines are indicated by the brackets marked A_1 , A_2 , and A_3 , corresponding to coupling constants of 8.0, 14.7, and 17.9 MHz. A low frequency peak without the complimentary high frequency partner is also seen, indicating another coupling constant of 2.8 MHz. In addition to these lines, a line marked with an arrow labeled ^{13}C is also shown. This resonance appears at the free precessional frequency of ^{13}C , and may be due to this isotope of carbon.

Kevan and colleagues were the first to publish ESE spectra of whole coal, and they demonstrated the power of the technique by analyzing the lineshape of the ^1H resonance (called the proton matrix line) [10]. Das, and later Doetschman, have reported ESE results in which proton hyperfine couplings of 4.8 and 14.0 MHz were seen in a low sulfur Pittsburgh bituminous coal [11,12]. Such hyperfine constants are consistent with protons in conjugated aromatic molecules, and provide direct evidence for the existence of such species in whole coal. They also are in good agreement with the constants measured by Retcofsky, et. al. using ENDOR spectroscopy on several Pennsylvania coals [13].

Not only can ESE spectroscopy obtain information about the molecular structure of organic compounds in coal, it can probe their environment. Figure 8 shows the magnetic field dependence of the amplitude of the 12.4 MHz component of the ESEEM pattern. It represents an "echo-induced" EPR spectrum of an Illinois #6 coal. The unique shape is due to a phenomenon called instantaneous diffusion, and can be related to the amplitude of the dipolar field experienced by an unpaired electron due to neighboring unpaired electrons [14]. Bowman and Clarkson have analyzed this effect and calculate it arises from a coal maceral with a radical concentration of 5×10^{18} spins/cm³, quite close to the average value EPR measurement of 1×10^{19} spins/cm³ for this coal [15].

Figure 9 illustrates the field dependence of two different frequency components of the ESEEM data from the Illinois #6. As we have already seen, the 12.4 MHz component has a lineshape characteristic of instantaneous diffusion. The 2.9 MHz peak, on the other hand, does not exhibit this effect, indicating that it arises from a coal maceral of lower radical concentration. The centers of the two spectra do not coincide, further indicating that the two signals have different g-values. The g-value difference between the two peaks, Δg , is nearly 0.001. Assuming that the principal mechanism for differences in g-values is the variation in heteroatom (O,N,S) content in different macerals, this data is consistent with a picture indicating that the 12.4 MHz coupling constant arises from a radical in a maceral with a significantly higher heteroatom content than

that found in the maceral containing the 2.9 MHz species. Such observations lead us to hope that in the future, ESE data can help us to develop maceral-specific information about the molecular forms present in whole coal.

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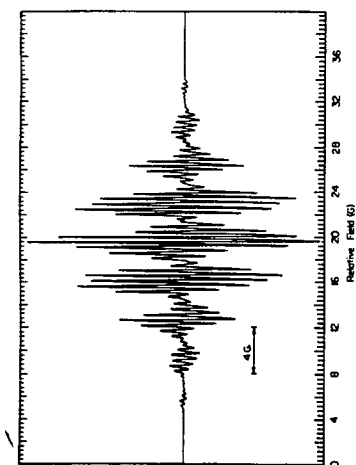


Figure 1. X-band EPR spectrum of the perylene cation radical in concentrated sulphuric acid.

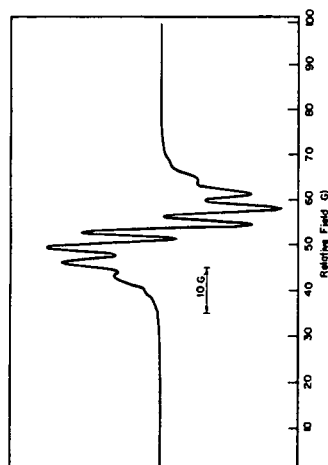


Figure 2. X-band EPR spectrum of the perylene radical adsorbed on alumina (115K)

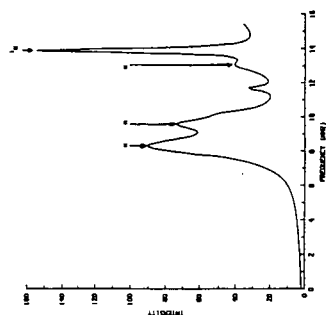


Figure 3. Processed ESE spectrum of the perylene radical adsorbed on alumina. Processing is through the LFQD version of Fourier transformation (see text) with conditioning to suppress features believed to be spurious. The three hyperfine transitions are marked with arrows labeled M. The peak marked $-H$ is the proton matrix line. $T = 15K$.

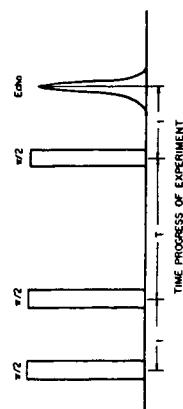


Figure 4. Timing diagram of the pulse sequence used to create a stimulated electron spin echo.

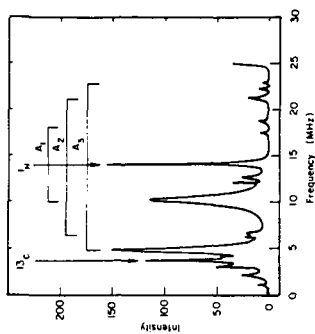


Figure 7. LFORD processed ESE spectrum of an evacuated sample of Illinois #6 whole coal. Resonances corresponding to the main proton hyperfine couplings are bracketed.

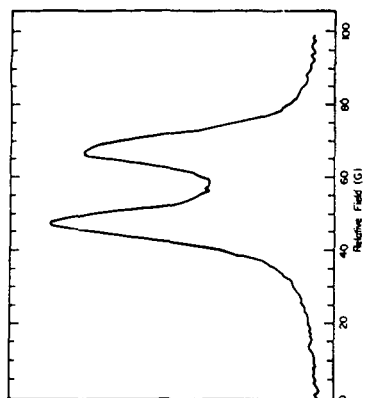


Figure 8. Plot of the magnetic field dependence of the amplitude of the 12.4 MHz modulation in the echo envelope of the evacuated Illinois #6 coal.

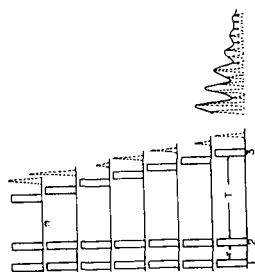


Figure 5. Diagram illustrating the formation of the ESEEM pattern in the context of a stimulated echo sequence. (after Kevan, [6])

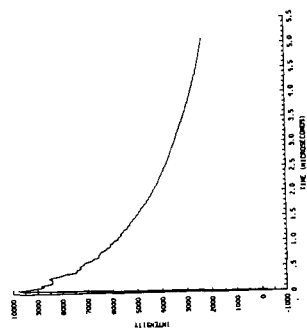


Figure 6. ESEEM effect in the echo envelope from an evacuated Illinois #6 whole coal. (15K).

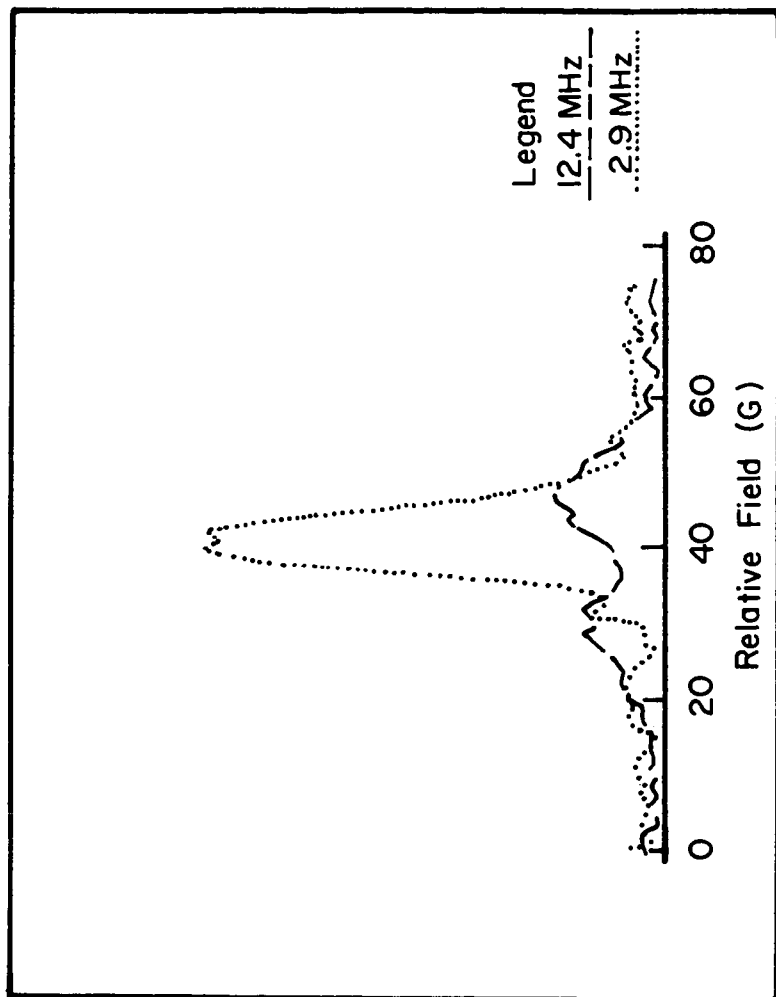


Figure 9. Plots of the magnetic field dependences of the amplitudes of the 2.9 and 12.4 MHz modulations in the echo envelope of the evacuated Illinois #6 whole coal.